Available online at www.sciencedirect.com

ScienceDirect

Energy Procedia 3 (2011) 84–91

Energy Procedia

www.elsevier.com/locate/procedia

E-MRS Fall Meeting 2010, Symposium C

Organic photovoltaic devices based on polyazomethine and fullerene

Marcin Palewicz[a,b,*], Agnieszka Iwan[b], Maciej Sibinski[c], Andrzej Sikora[b], Boleslaw Mazurek[b]

[a] *Institute of Electrical Engineering Fundamentals, Wroclaw University of Technology, 27 Wybrzeze Wyspianskiego Street, 50-370 Wroclaw, Poland*

[b] *Electrotechnical Institute Division of Electrotechnology and Materials Science, M. Sklodowskiej-Curie 55/61, 50-369 Wroclaw, Poland*

[c] *Department of Semiconductor and Optoelectronic Devices, Technical University of Lodz, Wolczanska 211/215 90-924 Lodz, Poland*

Abstract

The optical, structural and photovoltaic properties of a π-conjugated polyazomethine with siloxane linkages (PAZ1) were explored. Obtained poly (siloxane-azomethine) exhibited liquid crystalline properties and formed stable smectic A and nematic phases. PAZ1 was applied to organic solar cells construction as a donor, while [6,6]-phenyl C_{61} butyric acid methyl ester ($PC_{61}BM$) was used as an acceptor. The optical energy gap of PAZ1 at 2.24 eV was found. Atomic Force Microscope and photovoltaic experiments for devices based on PAZ1 and PAZ1:$PC_{61}BM$ as active layer were investigated. Power conversion efficiency of investigated devices were found in the range $(0.1 – 1) \cdot 10^{-2}$%.

Keywords: polyazomethines, liquid crystals, organic devices, photovoltaic devices, bulk heterojunction devices

1. Introduction

The development of polymers for photovoltaic applications is very attractive because polymers offer several significant advantages over their inorganic counterparts, i.e. ultrafast opto-electrical response, generation of charge on organic interface, modification of band gap, low cost synthesis, light and flexible devices and compatibility with various products, e.g. textiles. Because of large demanding of pure ecological electric energy has been started studies on new kinds of materials, which could be implemented to organic photovoltaic devices. One of the main streams has been focused on developing organic semiconductor conjugated polymers, which will have optical band gap below 2 eV, and also will be donor component. Nowadays following donor polymers are available in the market: polythiophenes (P3HT) [1-6], polymers with benzothadiazole unit [7-11], poly(p-phenylene vinylene)s (PPV) [12-17] and polycarbazoles [18]. That polymers have been characterized such parameters as regioregularity

* Corresponding author. Tel.:+4-871-328-3061; fax: +4-871-328-2551.
E-mail address: m.palewicz@iel.wroc.pl.

1876-6102
doi:10.1016/j.egypro.2011.01.014

(P3HT), good thermal and optical properties (PPV). Also for production and manufacturing of organic solar cells is very important easy preparation of each layer. Therefore counterchange polymers has been soluble in chloroform, 2,5-dimethyltetrahydrofuran and even in water (P3HT, PPV) what cause facile preparation of devices. Such material permit to make inexpensive bulk heterojunction (BHJ) active layer for organic solar cells based on donor polymer (P3HT or PPV) and acceptor component PCBM dissolved in chloroform or different medium. Also it has been possible to obtain bilayer organic solar cells based on mention polymer.

So far polyazomethine devices were investigated for photovoltaic applications only in two papers. Hindson et al. [19] investigated photovoltaic properties of triphenylamine-based polyazomethines obtained from 2,5-thiophenedicarboxaldehyde (Th), terephthalaldehyde (Ta) or 1,3-isophthalaldehyde (Iso) and 4,4'-diaminotriphenylamine (TPA). A photovoltaic device based on a TPA-Th/PCBM blend (1:3) under simulated STC (Standard Test Conditions) sunlight gives an open-circuit voltage (V_{OC}) of 0.41 V, a short-circuit current (J_{SC}) of 1.23 mA/cm^2 and a fill factor (FF) of 0.24, leading to a power conversion efficiency (PCE) of 0.12%. While for the TPA-Ta/PCBM blend (1:3) and TPA-Iso/PCBM blend (1:3) such photovoltaic parameters as V_{OC}, J_{SC}, FF and PCE have the following values, 0.42 V, 0.48 mA/cm^2, 0.22, 0.04% and 0.52 V, 0.19 mA/cm^2, 0.19, 0.02 %, respectively. Sharma et al. [20] studied photovoltaic properties of poly(phenyl azomethine furane) (PPAF) device with such construction as Ag/PPAF/ITO and received such value of photovoltaic parameters as V_{OC} = 1.2 V, J_{SC}, = 0.2 μA/cm^2, FF = 0.38 and PCE = 0.019%. Moreover, dendrimers with triphenylamine core were used as an active layer of Dye Sensitized Solar Cells (DSSC) [21,22].

In order to investigate the usefulness of poly(azomethine) with siloxane groups for photovoltaic applications we applied poly(siloxane-azomethine) (abbreviated hereinafter as PAZ1) with the structure shown in Figure 3. Siloxanes as flexible segments have been used in different polymeric structures in order to ameliorate the processing properties, due to their ability to lower the transition temperatures and enhance the solubility and high gas permeability [23-26]. Moreover, the siloxane unit reduces the crystallinity without destroying the liquid crystalline nature of the polymers [23-26]. This polymer constitutes a promising family of materials whose properties can be explored in various types of devices. Synthesis and mesomorphic properties of PAZ1 was the subject of our previous work [27]. This paper is devoted to optical (UV-Vis) and morphological (AFM) characterizations of new poly(siloxane-azomethine) and is summarized by photovoltaic experiments.

To best of our knowledge the poly(azomethine)s with siloxane units exhibiting liquid crystalline properties have not been investigated so far as polymers for photovoltaic applications.

2. Experimental

2.1. Polymer synthesis

PAZ1 was made using a one-step polycondensation technique without solvent and catalyst. 1 mmol of a poly(dimethylsiloxane)bis(3-aminopropyl)terminated and 1 mmol of 2,5-bis(hexyloxy)-1,4-bis(2,5-bis(hexyloxy)-4-formyl-phenylenevinylene)benzene was heated and stirred at 150°C for 20 hours. The mixture was then cooled to room temperature. The viscous polymer solution was washed (3 times) with hot methanol and next with hot acetone (3 times) and finally dried overnight at 50°C under vacuum.

UV-Vis absorption spectrum was recorded in solid state as film casted on quartz using spectrophotometer Jasco V670. Quartz substrates were purified using such organic solvents as chloroform and acetone. Characteristic parameters related with speed (880 turn per minute) and time (10 seconds) rotation were applied to spin-coating equipment. The surface morphology investigation of the PAZ1 was performed in air using a commercial Innova AFM system from Veeco Company. Measurements were done in Tapping Mode. Also inclination transformation of the topography data was made in order to provide better visibility of small features and details of the surface. Typical cantilever (about 40 N/m and <10 nm tip curvature) was used.

2.2. Device fabrication

Photovoltaic and AFM measurements were performed on ITO\PAZ1\Al and ITO\PEDOT:PSS\PAZ1:$PC_{61}BM$\Al with active area of about 25 cm^2. Schematic constructions of devices investigated in this work are presented in

Figure 1.

ITO-glass substrates were cleaned in ultrasonic cleaner at 15 minutes in acetone and after that in such organic solvents as isopropanol and acetone. The water solution of PEDOT:PSS (poly(3,4-ethylenedioxythiophene:poly(styrenesulfonate)) layer with the structure presented in Figure 3 was spread on ITO substrate using spin–coating equipment with rotating speed about 3000 turns per minute for 15 seconds.

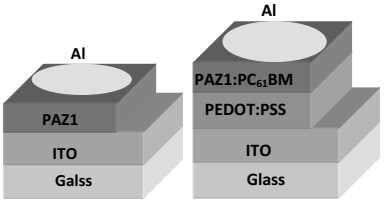


Figure 1: Schematic structure of reference sample (a) and investigated organic solar cells (b).

Thin organic layers based on polyazomethine PAZ1 or mixture PAZ1:$PC_{61}BM$ in weight ratio 1:1, 1:2 or 2:1 were dissolved at chloroform and spread subsequently. The active layers based on PAZ1 or PAZ1:$PC_{61}BM$ (called blend) was spin-coated onto ITO-covered glass substrate or ITO/PEDOT:PSS substrate with angular speed 900 turn per minute by 10 seconds at room temperature. Al electrode (about 6.75 cm^2 area) was prepared on the azomethine film surface by thermal evaporation method at pressure of $5 \cdot 10^{-4}$ Torr.

2.3. General description of measurement photovoltaic setup

I-V characteristics and parameters were obtained by the help of integrated measurement setup, calibrated for STC conditions (AM1.5G, 1000 W/m^2 and room temperature 25°C) according to international standards (IEC 60904-1 [28] and IEC 60904-3 [29]). Measurement setup consists of solar simulator equipped with four xenon bulbs Xenophot HLX and water dispersion filter and digital data acquisition system. Solar simulator operates in C+ standard according to IEC 60904-9 norm [30] at surface of 100 cm^2. The light condition is controlled by auto-calibration system equipped with photocell and on-line regulated impulse power supply. The temperature may be stabilized by water thermostat with accuracy of 0.5°C.

2.4. Adaptation for polymer solar cells measurements

Towards effective measurements of polymer solar cells the adaptation of I-V tracer was needed. One-side contacting system, shown in Figure 2, with additional isolation of brass base contacts was elaborated. Additionally the measurement and simulation model was calibrated according to expected parameters of polymer device.

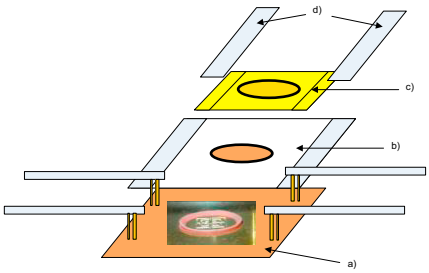


Figure 2. Adaptation of measurement setup for testing of one-side contacted cells: a) original measurement table with probes, b) isolating screen of the base brass contact, c) polymer bottom-contacted solar cell, d) additional emitter contacts for signal transferring.

3. Results and discussion

Poly(siloxane azomethine) PAZ1 was prepared using a simple one-step polycondensation procedure without solvent and catalysts [27]. Structure of the polymer presented in Figure 3 was confirmed by elemental analysis, FTIR and NMR spectroscopy [27].

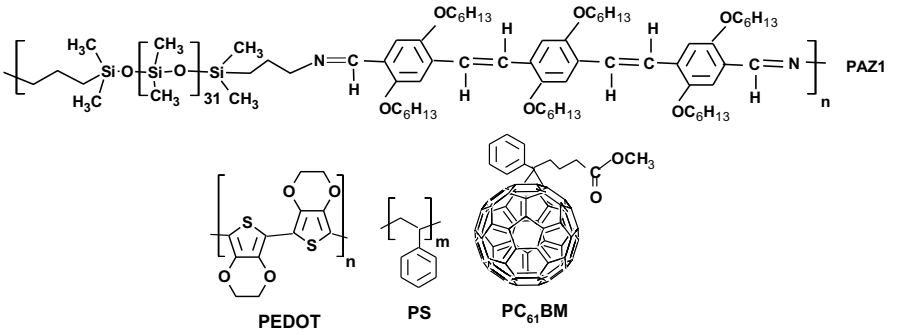


Figure 3. Chemical structure of polymer PAZ1, PEDOT, PSS and $PC_{61}BM$.

Polymer PAZ1 exhibited liquid crystalline properties [27]. Upon differential scanning calorimetry (DSC) analysis the polymer PAZ1 exhibited three enantiotropic transitions, such as crystal to smectic A (Cr/SmA), smectic A to nematic (SmA/N) and nematic to isotropic state (N/I) [27]. Polymer PAZ1 showed a liquid crystal to isotropic transition at 164 °C with a ΔH=2.8 J/g on the heating scan [27].

3.1 Optical measurements

Diluted PAZ1 solution was prepared in chloroform and spin coated on quartz slides for UV-Vis measurements and the results are shown in Figure 4. Energy band gap was calculated from absorption spectrum (E_g^{opt}) and absorption coefficient α ($E_g^{r=2}$). Absorption coefficient was used to indicate the kind of the transition. Absorption coefficient was obtained using equation:

$$\alpha = \frac{1}{d}\ln\left(\frac{(1-R)^2}{T}\right) \tag{1}$$

where: T - transmission, R – reflectivity, d film thickness. Thickness (d) of PAZ1 found about 250 nm thin layer spread on quartz substrate was calculated from reflectance measurements using Spectra Analysis program which is a subprogram of Spectra Manager (spectrophotometer Jasco V670).

To delimitate optical band gap from absorption (2) and absorption coefficient (3) following two equation were used:

$$E_g^{\ opt} = 1240/\lambda \tag{2}$$

$$\alpha \cdot E = A(E - E_g)^r \tag{3}$$

Energy band gap was calculated at index r equal to 2, what respond to indirect band to band transition. Energy band gap was appointed from linear approximation of absorption edge. Difference between value of energy gap detected from absorption spectrum and calculated absorption coefficient was very small and was found at 0.03 eV (see Figure 4). The UV-Vis spectrum of the PAZ1 exhibited one well defined absorption band at 425 nm, being responsible for π-π* transition in the imine group and is observed as well defined band. An instructive example of this approach is given in Figure 4.

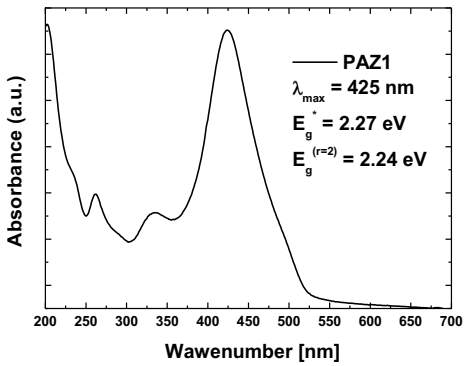


Figure 4. Absorption spectrum of PAZ1: maximum of absorbance (λ_{max}), energy bang gap calculated from absorption spectra (E_g^*) and absorption coefficient α ($E_g^{(r=2)}$).

3.2 AFM measurements

Atomic Force Microscope measurements were performed using tapping mode in order to reduce the influence of scanning tip of the surface. Experiments were conducted at room temperature on samples ITO\polymer (Figure 5 a, b), ITO\polymer:$PC_{61}BM$ (Figure 5 c, d) and ITO\PEDOT:PSS\polymer:$PC_{61}BM$ (Figure 5 e - j). In all cases the organic active layers made from polymer or polymer:$PC_{61}BM$ material based on ITO or ITO\PEDOT:PSS substrate were studied. The tip's oscillation amplitude was at level of a few nanometers. After the scanning process the presence of very small traces (nanosize) was detected. No topography or phase imaging signals revealed any significant trace of the scanning tip influence. Images of the polymer and polymer:$PC_{61}BM$ are presented in Figure 5.

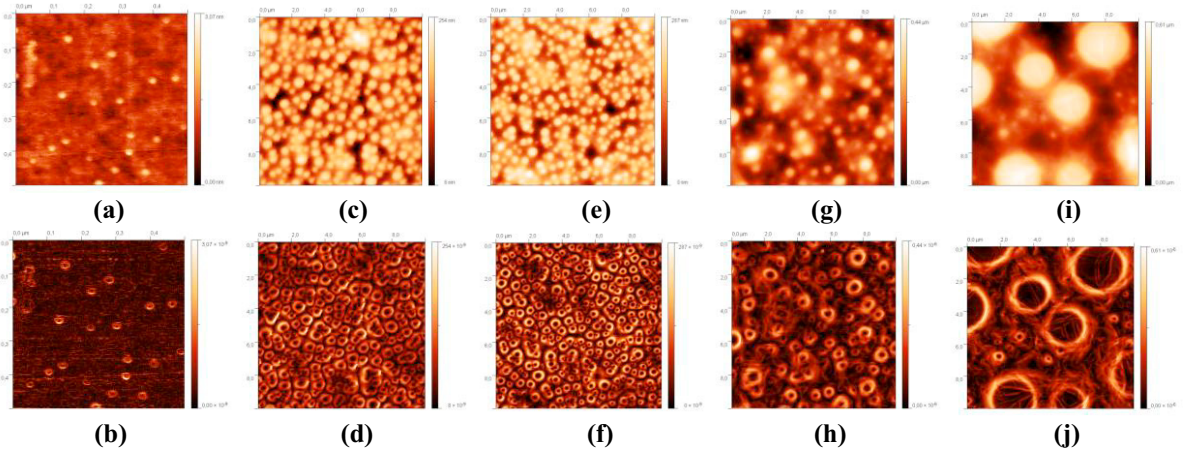


Figure 5. AFM images of PAZ1 (a, b) and PAZ1:$PC_{61}BM$ in weight ratio 1:1 (c - f), 1:2 (g, h) and 2:1 (i, j). Topography (top) processed with inclination transformation (bottom) are presented.

The thin films of the PAZ1 on the ITO or ITO\PEDOT:PSS substratum presented a homogenous surface. Characteristic granulation was typical for the polymers and polymer:fullerene blend thin layers and also aggregates were clearly visible in Figure 5. After the topography was measured, one can extract certain data describing the properties of the surface. Most popular values are roughness (R_a, R_{ms}). It was useful however to used in addition

another values as skew (the unbalance of height distribution maximum) and kurtosis (the peak's width on height distribution). Mentioned values for two investigated surface are presented in Table 1.

Table 1. The surface parameters of PAZ1 and PAZ1:$PC_{61}BM$.

Code	Surface statistics*				
	Ra [nm]	Rms [nm]	Skew	Kurtosis	Surface Area Ratio
ITO/PAZ1	0.68	1.0	12	431	1.000
ITO/PAZ1:$PC_{61}BM$ (1:1)**	31.9	39.4	-0.36	-0.15	1.037
ITO/PEDOT:PSS/PAZ1:$PC_{61}BM$(1:1)**	38.4	47.0	-0.30	-0.33	1.056
ITO/PEDOT:PSS/PAZ1:$PC_{61}BM$(1:2)**	55.8	71.9	0.67	0.51	1.035
ITO/PEDOT:PSS/PAZ1:$PC_{61}BM$(2:1)**	125.2	145.4	0.32	-1.06	1.032
* values calculated for scanning field 10 μm × 10 μm (100 μm^2 scan area)					
** weight ratio of polymer to $PC_{61}BM$ component					

Moreover it was possible to calculate dimension of granulated polymers and polymer:fullerene blend on substratum from images presented in Figure 5 a-j. Magnitude of lump for investigated materials was in range from about 20 nm to 3 μm. We suppose that scale of the granulated polymer and polymer:fullerene blend concentration was related with a porosity of the substratum, quality of arise PEDOT:PSS interlayer, weight ratio of polymer to fullerene component and technological parameters implemented to spin-coater equipment.

3.3 Photovoltaic measurements

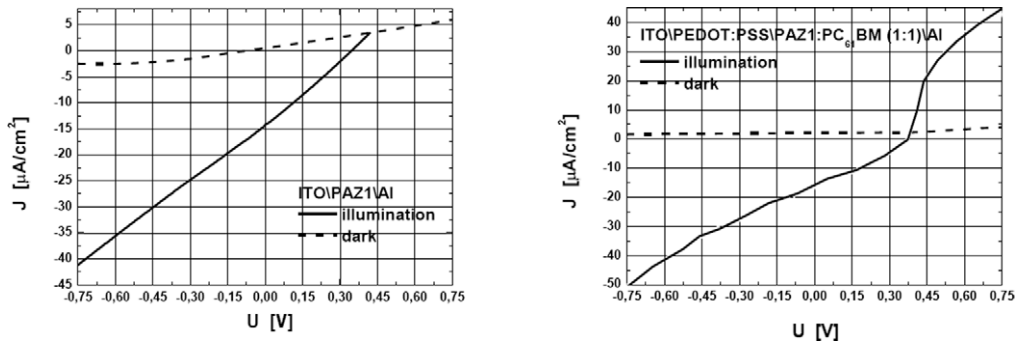
Photovoltaic experiments were made under STC conditions (AM1.5G, 1000 W/m^2 and room temperature 25 °C) for the bulk heterojunction devices (BHJ) such as ITO\PEDOT:PSS\PAZ1:$PC_{61}BM$\Al and compare with reference device ITO\PAZ1\Al. PAZ1 was blended with [6,6]-phenyl C_{61} butyric acid methyl ester ($PC_{61}BM$) in the weight ratio 1:1, 1:2 and 2:1. Blending conjugated polymers with electron acceptors, e.g. fullerenes are efficient way to break apart photoexcited excitons into free charge carriers. Basing on these results open circuit voltage (V_{OC}), short circuit current (J_{SC}), fill factor (FF) and power conversion efficiency (PCE) were obtained. The ranges of measurements were adjusted experimentally for each cell and the final outcomes were the mean values of ten measurements in each point. A summary of the device performance are presented in Table 2. Current density – voltage characteristics are shown in Figure 6.

Table 2. Photovoltaic parameters of organic solar cells based on PAZ1 and PAZ1: $PC_{61}BM$.

Code	J_{sc} [μA\cm^2]	V_{oc} [V]	FF [-]	PCE [$\cdot 10^{-2}$ %]
ITO\PAZ1\Al	14.31	0.35	0.15	0.07
ITO\PEDOT:PSS\PAZ1:$PC_{61}BM$(1:1)\Al	15.84	0.37	0.22	0.1
ITO\PEDOT:PSS\PAZ1:$PC_{61}BM$(1:2)\Al	16.36	0.75	0.75	0.9
ITO\PEDOT:PSS\PAZ1:$PC_{61}BM$(2:1)\Al	17.12	0.75	0.13	0.16

Obtained results confirm the photovoltaic effects in all tested constructions. Measured efficiencies were low and was found in the range (0.07-0.9) · 10^{-2}% depending on the device construction and weight ratio of PAZ1 to $PC_{61}BM$ (Table 2). Fullerenes and PEDOT:PSS influences positively on the photovoltaic parameters. The highest value of PCE (about 0.01%) and FF (0.75) was obtained for the device ITO\PEDOT:PSS\PAZ1:$PC_{61}BM$\Al with the weight ratio 1:2 (Table 2). However the highest value of short circuit current density (J_{SC} = 17.12 μA\cm^2) was obtained for device ITO\PEDOT:PSS\PAZ1:$PC_{61}BM$\Al with the weight ratio 2:1. There are several reasons for

such behavior. PAZ1 is not fully conjugated and we attribute the poor photovoltaic performance to difficulty in charge hopping between monomer units.



(a) **(b)**

Figure 6. Photovoltaic curves of (a) ITO\PAZ1\Al and (b) ITO\PEDOT:PSS\PAZ1:$PC_{61}BM$\Al in weight ratio 1:1.

As one of the obvious reasons of very low value of efficiencies, high series resistance may be identified. For further experiments several features of the cells should be improved. Among them better quality of the ITO and metallic contacts is needed for higher test reliability. It is clear that the PAZ1 is probably promising material for photovoltaic applications. The first reason for this statement is well solubility of PAZ1 in such solvents as chloroform or 1,2-dichloroethane. The second, PAZ1 exhibited liquid crystalline properties and their properties can help in the self-organization of polymer chain in the constructed devices and influence on photovoltaic properties of the polymer. Our photovoltaic results in comparison with the results obtained by Hindson et al. [19] (PCE = 0.02 % to 0.12 %) and Sharma et al. [20] (0.019%) suggested that it is very attractive to used as a donor poly(siloxane-azomethine) with liquid crystalline properties in the construction of BHJ devices.

4. Conclusion

Photovoltaic experiments were made under STC conditions (AM1.5G, 1000 W/m^2 and room temperature 25 °C) for the bulk heterojunction devices (ITO\PEDOT:PSS\PAZ1:$PC_{61}BM$\Al) and compared with reference device (ITO\PAZ1\Al). Power conversion efficiencies (PCE) of investigated devices were found in the range 0.001-0.01% depend on the device construction and weight ratio of PAZ1 to $PC_{61}BM$. The highest PCE at about 0.01% was found for device based on PAZ1:$PC_{61}BM$ in the weight ratio 1:2. Our study suggests therefore a potential new application of poly(siloxane azomethine)s by exploiting their liquid crystalline and transport properties, paving the way toward stable organic optoelectronic devices.

Acknowledgements

This work was financial supported in the frame of expenditure on science (2010-2011) No. NN510 191538.

References

[1] B.C. Thompson, M.J. Frechet, Angew. Chem. Int. Ed. 47 (2008) 58.
[2] N. Blouin; M. Leclerc, Acc. Chem. Res. 41 (2008) 1110.
[3] R.D. McCullough, R.D. Lowe; M. Jayaraman, D.L. Anderson, J. Org. Chem. 58 (1993) 904.
[4] T.A. Chen, R.D. Reike, J. Am. Chem. Soc. 114 (1992) 10087.
[5] M. Reyes-Reyes; K. Kim, J. Dewald, R. Lopez-Sandoval, A. Avadhanula, S. Curran, D.L. Carroll, Org. Lett. 7 (2005) 5749.

[6] G. Li, Y. Yang, R.A.B. Devine, C. Mayberry, Nanotechnology 19 (2008) 424014.

[7] C.J. Brabec, C. Winder, N.S. Sariciftci, J.C. Hummelen, A. Dhanabalan, P.A. van Hal, R.A.J. Janssen, Adv. Funct. Mater. 12 (2002) 709.

[8] F. Zhang, M. Ceder, O. Inganäs, Adv. Mater. 19 (2007) 1835.

[9] A. Gadisa, K. Tvingstedt, S. Admassie, L. Lindell, X. Crispin, M.R. Andersson; W.R. Salaneck, O. Inganas, Synth. Met. 156 (2006) 1102.

[10] R. Yang, R. Tian, J. Yan, Y. Zhang, J. Yang, Q. Hou, W. Yang, C. Zhang, Y. Cao, Macromolecules 38 (2005) 244.

[11] S.H. Park, A. Roy, S. Beaupre, S. Cho, N. Coates, J.S. Moon, D. Moses, M. Leclerc, K. Lee, A.J. Heeger, Nat. Photonics 3 (2009) 1.

[12] J.L. Maldonado, G. Ramos-Ortíz, M.L. Miranda, S. Vázquez-Córdova; M.A. Meneses-Nava, O. Barbosa-García, M. Ortíz-Gutiérrez, Am. J. Phys. 76 (2008) 1130.

[13] J. Luo, H. Wu, C. He, A. Li, W. Yang, Y. Cao, Appl. Phys. Lett. 95 (2009), 043301-1.

[14] L. Yan, H. Yan-Bing, J. Hui, S. Quan-Min, L. Jun, S. Xin, C. Xiao-Wie, Chin. Phys. Lett. 24 (2007) 818.

[15] J. Davenas, P. Alcouffe, A. Ltaief, A. Bouazizi, Macromol. Symp. 233 (2006) 203.

[16] M.E.D. Ayuk; L.H. Nguyen, K. Schmidtke, A. Wild, C. Sieber, S. Guenes, N.S. Sariciftci, J. Polym. Sci.: Part A: Polym. Chem. 45 (2007) 1619.

[17] P. Atienzar, T. Ishwara, M. Horie, J.R. Durrant, J. Nelson, J. Mater. Chem. 19 (2009) 5377.

[18] J.V. Grazulevicius, P. Strohriegl, J. Pielichowski, K. Pielichowski, Prog. Polym. Sci. 28 (2003) 1297.

[19] J.C. Hindson, B. Ulgut, R.H. Friend, N.C. Greenham, B. Norder, A. Kotlewski, T.J. Dingemans J. Mater. Chem. 20 (2010) 937.

[20] G.D. Sharma, S.G. Sandogaker, M.S. Roy, Thin Solid Films 278 (1996) 129.

[21] T. Nakashima, N. Satoh, K. Albrecht, and K. Yamamoto, Chem. Mater. 20 (2008) 2538.

[22] K. Yamamoto, K. Takanashi, Polymer 49 (2008) 4033.

[23] T. Ganicz, W.A. Stanczyka, E, Białecka-Florjanczyk, I. Sledzinska, Polymer 40 (1999) 4733.

[24] J. T. Sołtysiak, E. Białecka-Florjanczyk, J. Przedmojski, Europ. Polym. J. 42 (2006) 1662.

[25] T. Ganicz, T. Pakula, W. Fortuniak, E. Białecka-Florjanczyk, Polymer 46 (2005) 11380.

[26] Y. Poojari, S.J. Clarson, Macromolecules, doi: 10.1021/ma100548z.

[27]. A. Iwan, E. Schab-Balcerzak, M. Palewicz, H. Janeczek, Effect of Siloxane Units on Thermal, Optical and Electrical Properties of New Poly(azomethine)s and Poly(imide)s, Polymer J. (sent to journal).

[28] IEC 60904-1 Photovoltaic devices – Part 1: Measurement of PV current-voltage characteristics.

[29] IEC 60904-3 Photovoltaic devices – Part 3: Measurement principles for terrestrial photovoltaic (PV) solar devices with reference spectral irradiance data.

[30] IEC 60904-9 Photovoltaic devices – Part 9: Solar simulator performance requirements.